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Anionic Polymerizations of 2-Vinylbenzoxazole and 2-Isopropenylbenzoxazole

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ABSTRACT: Anionic polymerizations of 2-vinylbenzoxazole (**1**) and 2-isopropenylbenzoxazole (**2**) were carried out in THF at −78 °C with (diphenylmethyl)potassium and (1,1-diphenyl-3-methylpentyl)lithium. The poly(**1**)s having broad molecular weight distributions ($M_w/M_n > 1.5$) were always obtained in rather low yields both after 1 h of polymerization and even after 24 h. On the other hand, the polymerization of **2** proceeded quantitatively with each initiator within 1 h and the resulting poly(**2**)s possessed the predicted molecular weights and narrow molecular weight distributions ($M_w/M_n < 1.1$). The persistency of the propagating carbanion of poly(**2**) was demonstrated by a quantitative initiation efficiency in the postpolymerization of **2**. These results strongly indicate that the anionic polymerization of **2** affords a stable living polymer. Novel block copolymers, poly(**2**-*b*-*tert*-butyl methacrylate), poly(**2**-*b*-*tert*-butyl methacrylate-*b*-**2**), and poly(**2**-*b*-styrene-*b*-**2**), were successfully synthesized by the sequential block copolymerization of **2** and comonomers.

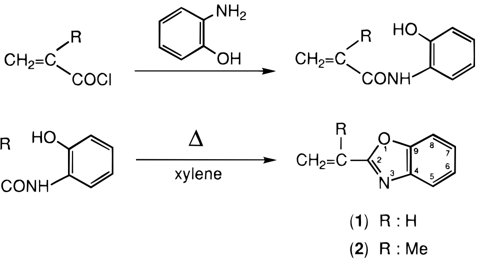
Introduction

It is well-known that anionic living polymerization gives tailored polymers in which the number-average degrees of polymerization are controlled by the molar ratios of monomers to initiators. The molecular weight distributions (MWD) of the resulting polymers are usually very narrow; M_w/M_n values are typically regulated within 1.1. Furthermore, well-defined block copolymers and end-functionalized polymers can be synthesized by using anionic living polymerization. Thus, the anionic polymerization system is a powerful tool to prepare the polymers having the predictable molecular structures controlled strictly.[1] Unfortunately, the monomer examples which can form anionic living polymers have been restricted to styrene, α-methylstyrene, 1,3-butadiene, isoprene, and some alkyl methacrylates until the beginning of the 1980s.

For this decade, the anionic living polymerizations of many vinyl monomers having a wide variety of useful functional groups have been newly found.[2] Our examples discovered are the styrene derivatives containing protected functional groups,[3] reactive silyl groups,[4] and electron-withdrawing groups,[5] 2-silyl-substituted 1,3-butadienes,[6] and methacrylates bearing useful functionalities.[7] The discovery of living polymerizations of some alkyl (meth)acrylates[8] and vinyl phenyl sulfoxide[9] is also a recent topic in this field. Moreover, *N*,*N*-dialkylacrylamides[10] and acrylonitrile[11] are suggested to give the polymers having controlled chain lengths under anionic conditions.

Heterocyclic compounds are known to play an important role in the field of organic chemistry, occur widely in nature, and enjoy wide application in a variety of commercially important products such as pharmaceuticals and flavor and fragrance compounds. Recently, the vinyl polymers containing heterocycles have received considerable attention, since they show interesting chemical and physical properties due to their polarity and abilities to form hydrogen bonding.[12] With respect to anionic living polymerization of vinyl heterocycles, the polymerization of vinylpyridine derivatives such as 2-vinyl-[13] and 4-vinylpyridines[14] and 2-isopropenylpyridine[15] is the only known successful example so far. Although numerous vinyl heterocycles have been synthesized and polymerized with cationic or free-radical initiators,[16] little attention has been paid to the controllable anionic polymerization up to the present time. We will therefore start a new series of study on the anionic polymerization of vinyl heterocycles. As a first report of this series, we herein report the anionic polymerization of 2-vinylbenzoxazole (**1**) and 2-isopropenylbenzoxazole (**2**).

Scheme 1



The oxazole moieties are known to show specific reactivity to the quaternization and the Diels−Alder reaction as an aza diene[17] and serve as luminescent materials.[18] Those frameworks are also contained in some of the important synthetic dyes and in the bio-related compounds.[19] Thus, the vinyl polymers bearing oxazole functionalities will be expected to show interesting reactivities and properties as new materials.

The focuses of this study are to clarify the polymerization behaviors of **1** and **2**, especially from the viewpoint of the anionic living polymerization and to elucidate the reactivities of the monomers and the living polymers under anionic conditions.

Results and Discussion

The monomers employed in this study, **1** and **2**, were synthesized by a two-step reaction of 2-aminophenol and (meth)acryloyl chloride, as shown in Scheme 1. It was reported that the lithiation of 2-methylbenzoxazole readily occurred at the methyl substituent with organolithium reagents such as *n*-butyllithium and lithium diisopropylamide in THF at −78 °C.[20] The resulting

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Table 1. Anionic Polymerization of 1 in THF at −78 °C

run	amount of **1**, mmol	initiator; amt, mmol	amt of DPE,[a] mmol	amt of LiCl, mmol	time, h	yield, %	$10^{-3}M_n$ calcd[b]	$10^{-3}M_n$ SEC[c]	M_w/M_n[c]
1	3.05	Li-Naph;[d] 0.0995	0.205		1	81	7.7	4.7	1.52
2	3.84	*s*-BuLi; 0.0678	0.151		24	100	8.4	6.8	1.48
3	3.45	*s*-BuLi; 0.0768	0.107	0.300	1	58	3.9	3.1	1.33
4	3.11	*s*-BuLi; 0.0546	0.118	0.276	24	33	2.8	2.8	1.47
5	3.66	K-Naph;[e] 0.0882	0.185		1	40	5.1	3.4	1.83
6	3.34	K-Naph; 0.0857	0.123		24	48	5.7	6.7	1.74

[a] 1,1-Diphenylethylene. [b] M_n(calcd) = [monomer] × (MW of monomer) × f/[initiator] + MW of initiator; f = 1 or 2, corresponding to the functionality of the initiators. [c] M_n(SEC) and M_w/M_n were obtained by SEC calibration using standard poly(methyl methacrylate)s in THF solution. [d] Lithium naphthalenide. [e] Potassium naphthalenide.

lithiated product is recognized as a model for a terminal propagating carbanion derived from 2-vinylbenzoxazoles. It is apparently stabilized by both the electron-withdrawing effect of the benzoxazole ring and the extended π-conjugated system containing the benzoxazole ring, indicating that the propagating chain end from **1** is stable. Therefore, we will expect the anionic polymerizations of **1** and **2** to proceed without serious side reactions.

Anionic Polymerization of 1. Anionic polymerization of **1** was carried out in THF at −78 °C for 1 h. The anionic initiators involved (1,1-diphenyl-3-methylpentyl)lithium and [1,1,4,4-tetraphenylbutanediyl]dilithium and -dipotassium. When **1** was added to each of the initiators, the polymerization system immediately showed a clear yellow color. No change of coloration was observed during the polymerization, but the yellow coloration rapidly disappeared by adding a small amount of methanol to terminate the polymerization. The polymer was precipitated upon pouring the reaction system into a large excess of hexane. The polymer was purified by the reprecipitation in a THF/hexane system and by freeze-drying from the benzene solution. From the spectroscopic analyses (^{1}H and ^{13}C NMR and IR) of the polymer, it was confirmed that the vinyl polymerization of **1** proceeded exclusively under the conditions and no cleavage of the benzoxazole moiety occurred.

Table 1 shows the polymerization results of **1** at −78 °C in THF. By using [1,1,4,4-tetraphenylbutanediyl]dilithium, poly(**1**) was obtained in 81% yield after 1 h of polymerization. The size exclusion chromatography (SEC) analysis of the polymer indicated that the molecular weight distribution (MWD) is unimodal but relatively broad, the polydispersity index (M_w/M_n) being 1.52. After the polymerization system was allowed to stand for 24 h at −78 °C, the polymerization of **1** was completed and poly(**1**) with a similarly broad MWD (M_w/M_n = 1.48) was produced (Figure 1A). Although the rate of polymerization of **1** was remarkably lowered by the addition of lithium chloride,[8a] there was no effect on the MWD of the polymer. With [1,1,4,4-tetraphenylbutanediyl]dipotassium (run 5 and 6), the yields of the poly(**1**)s were far from quantitative even after 24 h and the distributions of the molecular weights were very broad. Thus, the results of polymerization employed initiators associated with the potassium countercation were more disappointing from the viewpoint of control of the MWD. As a result, although the anionic polymerization of **1** unequivocally proceeds, it is considered that some side reactions take place during the polymerization of **1** under the conditions employed here. For the plausible explanation of the side reaction, we now speculate that the α-proton abstraction of the main chain in the produced poly(**1**) occurs to some extent, as shown in Scheme 2. We have therefore introduced the methyl group into the vinyl group of **1** at the α-position to suppress the proton abstraction, and a new monomer, 2-isopropenylbenzoxazole (**2**), is synthesized to anionically polymerize under conditions identical to those of **1**.

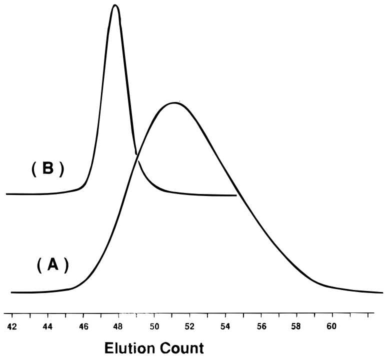
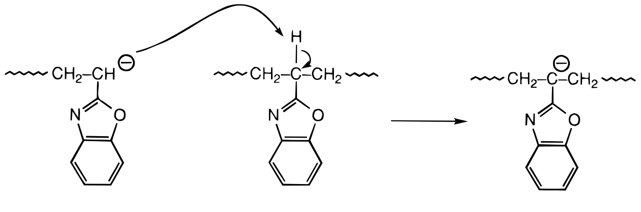


Figure 1. SEC curves of poly(**1**) obtained with *s*-BuLi/DPE at −78 °C (A), M_n(SEC) = 6800, M_w/M_n = 1.48 (Table 1, run 2), and poly(**2**) obtained with *s*-BuLi/DPE at −78 °C (B), M_n(obsd) = 24 000, M_w/M_n = 1.07 (Table 2, run 10).

Scheme 2



Anionic Polymerization of 2. Anionic polymerization of an alternative monomer, **2**, was carried out under conditions similar to the cases of **1**. The initiators employed were (1,1-diphenyl-3-methylpentyl)lithium, (diphenylmethyl)potassium, (triphenylmethyl)potassium, [1,1,4,4-tetrakis[4-(trimethylsilyl)phenyl]butanediyl]dipotassium,[21] and potassium *tert*-butoxide. The reaction mixture of **2** always showed a clear yellow (Li^+) or orange (K^+) coloration during the course of the polymerization. The coloration remained at −78 °C even after 24 h and disappeared immediately with a small amount of methanol, indicating the existence of the propagating carbanions. The reaction mixture was poured into a large excess of methanol for precipitation of a polymeric product. After purification, the yielding polymer was characterized by ^{1}H and ^{13}C NMR and IR spectroscopies. The spectroscopic information strongly supported that the vinyl polymerization of **2** exclusively proceeded to afford a poly(**2**) of the expected repeating chain structure.

The polymerization results of **2** are summarized in Table 2. At −78 °C with (1,1-diphenyl-3-methylpentyl)lithium, (diphenylmethyl)potassium, and [1,1,4,4-tetrakis[4-(trimethylsilyl)phenyl]butanediyl]dipotassium, the polymerizations of **2** were always complete

Table 2. Anionic Polymerization of 2 in THF for 1 h[a]

run	temp °C	amt of **2**, mmol	initiator; amt, mmol	amt of DPE,[b] mmol	amt of LiCl, mmol	$10^{-3}M_n$ calcd[c]	SEC[d]	obsd[e]	M_w/M_n[d]
7	−78	3.30	*s*-BuLi; 0.0563	0.113		9.3	6.0	10	1.09
8	−78	2.74	*s*-BuLi; 0.0501	0.118	0.212	8.7	6.1	10	1.07
9[f]	−78	4.62	*s*-BuLi; 0.0765	0.120		9.9	7.5	12	1.06
10	−78	5.20	*s*-BuLi; 0.0329	0.104		26	14	24	1.07
11	−30	3.89	*s*-BuLi; 0.0243	0.168		26	20	30	1.06
12	0	3.60	*s*-BuLi; 0.0473	0.153		12	10	16	1.21
13	−78	2.14	K-Naph;[g] 0.0897	0.151[h]		8.2	5.0	8.8[i]	1.12
14	−78	3.69	K-Naph; 0.0703	0.132[h]		17	10	16[i]	1.10
15	−78	3.95	K-Naph; 0.0460	0.0870[h]		28	15	23[i]	1.11
16	−78	4.38	Ph_2CHK;[j] 0.0442			16	11	17	1.08
17	−78	2.96	Ph_3CK;[k] 0.0882			5.3	3.1	6.1	1.09
18	−78	4.27	Ph_3CK; 0.0737			9.4	4.6	8.3	1.08
19	−78	3.79	*t*-BuOK; 0.0243			1.9	52	76	1.04

[a] Yields of polymers were almost quantitative in each case. [b] 1,1-Diphenylethylene. [c] M_n(calcd) = [monomer] × (MW of monomer) × *f*/[initiator] + MW of initiator; *f* = 1 or 2, corresponding to the functionality of the initiators. [d] M_n(SEC) and M_w/M_n were estimated from the SEC calibration using standard poly(methyl methacrylate)s in THF solution. [e] M_n(obsd) was determined by the SEC calibration for poly(**2**) in THF. [f] For 5 min. [g] Potassium naphthalenide. [h] 1,1-Bis(4-(trimethylsilyl)phenyl)ethylene. [i] M_n(obsd) was determined by the end group analysis using ^{1}H NMR. [j] (Diphenylmethyl)potassium. [k] (Triphenylmethyl)potassium.

within 1 h to give the polymers in quantitative yields, in contrast to the cases of **1**. The SEC analyses of the poly(**2**)s demonstrated the unimodal and sharp chromatograms. The M_w/M_n values were around 1.1, indicating very narrow MWDs (Figure 1B). All the molecular weights estimated by SEC always deviated from the calculated values based on the molar ratios of monomer to initiators. The molecular weights by SEC in THF presented values approximately two-thirds of the calculated ones. By contrast, the molecular weights determined by the end group analysis using ^{1}H NMR spectroscopy agreed well with the calculated values, as expected (Table 2, runs 13−15).[21] This shows that the M_n values of poly(**2**), estimated from SEC calibration using the standard poly(methyl methacrylate)s in THF, are underestimated, probably due to the difference of hydrodynamic volumes of the polymers. By using a calibration between the M_n values by ^{1}H NMR and by SEC, molecular weights of other homopoly(**2**) samples were determined, as shown in Table 2. From these results, it is demonstrated that all the polymers of **2** prepared at −78 °C possess the predicted molecular weights and narrow MWDs. These results for **2** are in sharp contrast to the polymerization behavior of the 2-vinyl counterpart, **1**, as shown in the preceding section. The introduction of a methyl group on the vinyl α-carbon of **1** remarkably improves the polymerization behavior of **2** to attain the living polymerization.

In the polymerization at −30 °C, a polymer of a well-controlled chain structure was still obtained quantitatively. By contrast, when the polymerization temperature was raised to 0 °C, the SEC curve of the polymer showed a long tailing and a broadening of the MWD (M_w/M_n = 1.21), which occurred probably due to the undesirable side reactions of the propagating species during the propagation. Thus, for accurate control of the polymerization for **2**, the reaction temperature should be restricted below 0 °C.

The initiation with less nucleophilic (triphenylmethyl)potassium (Ph_3CK) at −78 °C gave the poly(**2**)s having the controlled M_n's in addition to the narrow MWDs. In this case, the efficiency of the initiator is also quantitative. Interestingly, a poly(**2**) with a very narrow MWD was quantitatively obtained with potassium *tert*-butoxide (*t*-BuOK) at −78 °C for 2 h, whereas the observed molecular weight largely deviated from the calculated value. The initiation efficiency of this polymerization can be estimated to be only 3% from the molecular weight of the resulting poly(**2**). It is realized that both *t*-BuOK and Ph_3CK are not sufficiently nucleophilic to initiate the polymerization of styrene at all but each nucleophile can react with alkyl methacrylates to give the polymers. This suggests that anionic polymerizability of **2** is comparable to those of alkyl methacrylates, as discussed in detail later.

To investigate the living nature of the propagating carbanion at −78 °C, the postpolymerization of **2** was carried out with Ph_3CK as an initiator. The second-stage polymerization of **2** proceeded with quantitative efficiency to produce a post-poly(**2**) with a predicted M_n and a narrow MWD by the addition of the second feed of **2** to the THF solution of pre-poly(**2**) prepared at −78 °C for 1 h. This indicates that the carbanion derived from **2** is completely stable at −78 °C for 1 h and also suggests the feasibility of the living poly(**2**) for the tailored synthesis of block copolymer by the sequential copolymerization under the employed conditions.

It is concluded that the polymerization of **2** proceeds in a living fashion to give the polymers of known molecular weights and narrow MWDs. On the other hand, the anionic polymerization of **1** is accompanied with the side reaction, the acidic α-methine proton abstraction from the produced poly(**1**). This type of side reaction is well-known in the anionic polymerization of alkyl acrylates to result in the incompletion of the polymerization and the broadening of the MWD.[22] Substitution of the methyl group on the α-carbon drastically changes the polymerization behavior of **2** from that of **1** under anionic conditions to avoid the side reactions, as was observed in the polymerization of alkyl methacrylates.

Block Copolymerizations of 2 with Styrene and *tert*-Butyl Methacrylate. From the synthetic point of view, attainment of the anionic living polymerization of **2** in the preceding section enables us to prepare novel tailored block copolymers containing the heterocyclic benzoxazole moiety. In addition to this, the relative reactivities of **2** and the terminal carbanion of the resulting living polymer will also be elucidated from the results of block copolymerization with styrene and *tert*-butyl methacrylate (tBMA).

At first, a synthesis of triblock copolymer of styrene (first monomer) and **2** (second monomer) was attempted by the sequential polymerization with potassium naphthalenide in THF at −78 °C. To a polymerization system of difunctional living polystyrene associated with

Table 3. Block Copolymerization of 2 with Styrene and *tert*-Butyl Methacrylate (tBMA) at −78 °C in THF[a]

				block copolymer (homopolymer[b])		
				$10^{-3}M_n$		
run	block sequence	A monomer	B monomer	calcd[c]	obsd[d]	M_w/M_n[e]
20	A−B−A	2	styrene	21 (10)	22 (8.6)	1.08 (1.08)
21	A−B−A	2	tBMA	23 (12)	21 (11)	1.09 (1.12)
22[f]	B−A−B	2	styrene	23 (10)	11[f](11)	1.12[f](1.12)
23	A−B	2	tBMA	28 (9.4)	24 (8.3)	1.09 (1.08)

[a] Yields of polymers were nearly quantitative in each case except for run 22. [b] Homopolymers were obtained at the first-stage polymerization. [c] M_n(calcd) = [monomer] × (MW of monomer) × f/[initiator] + MW of initiator; f = 1 or 2, corresponding to the functionality of the initiators. [d] The molecular weights of the block copolymers were determined by using the molecular weights of the homopolymers and the molar ratios of monomer units in the block copolymer analyzed by ^{1}H NMR. [e] M_w/M_n was obtained by SEC calibraton using standard polystyrenes in THF. [f] Homopoly(**2**) and unreacted styrene monomer were quantitatively recovered from the reaction mixture.

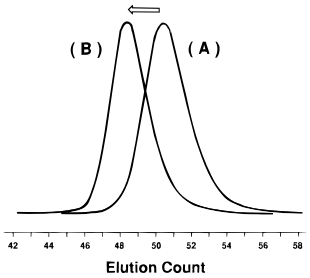


Figure 2. SEC curves of poly(tBMA) at the first-stage polymerization (A) and of poly(**2**-*b*-tBMA-*b*-**2**) obtained at −78 °C (B): peak A, M_n(obsd) = 11 000, M_w/M_n = 1.12; peak B, M_n(obsd) = 21 000, M_w/M_n = 1.09 (the second feed of monomer was added 2 h after the first-stage polymerization).

the potassium countercation was added **2**, and the system was allowed to react for a further 1 h. A change of the coloration was immediately observed from dark red to orange, indicating the rapid crossover reaction of **2** with the polystyryl anion. After termination with methanol, a polymer was quantitatively obtained. The ^{1}H NMR analysis of the product demonstrated that the segment composition of each polymer was identical to the feed ratio of styrene and **2**. The SEC trace of the copolymer remained sharp and unimodal and shifted to the higher molecular weight region after the addition of **2**. Table 3 shows a good agreement between the observed molecular weight of the copolymer and the theoretical value based on the living sequential copolymerization. Thus, the results obtained here show that the second-stage polymerization of **2** proceeded quantitatively to give a triblock copolymer, poly(**2**-*b*-styrene-*b*-**2**), having a predicted molecular weight and a narrow MWD.

Similarly, the sequential copolymerization of tBMA (first monomer) and **2** (second monomer) gave a triblock copolymer of the predicted molecular architecture by using oligo(α-methylstyryl)dipotassium as an initiator in THF at −78 °C. Figure 2 demonstrates the SEC curves of the starting homopoly(tBMA) and poly(**2**-*b*-tBMA-*b*-**2**) obtained. It can be clearly seen that the polymerization of **2** takes place in quantitative efficiency with the propagating species of living poly(tBMA), in keeping with the narrow MWD of the polymer (M_w/M_n = 1.09). It is known that the carbanion derived from tBMA cannot initiate the polymerization of styrene at all due to the low nucleophilicity under the identical conditions.[23] By contrast, the second-stage polymerization of **2** was quantitatively initiated with living poly(tBMA) to form a well-defined block copolymer, indicating a high polymerizability (electrophilicity) of **2**.

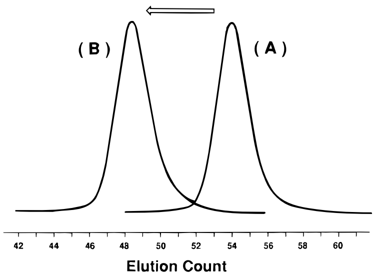


Figure 3. SEC curves of poly(**2**) at the first-stage polymerization (A) and of poly(**2**-*b*-tBMA) obtained at −78 °C (B): peak A, M_n(obsd) = 8300, M_w/M_n = 1.08; peak B, M_n(obsd) = 24 000, M_w/M_n = 1.09 (the second monomer was added 1 h after the first-stage polymerization).

Next, in order to elucidate the reactivity of the propagating carbanion of living poly(**2**), the sequential polymerization of styrene and tBMA was carried out with living poly(**2**) in THF at −78 °C. As a result, the living poly(**2**) could not initiate the further polymerization of styrene at all, and the starting homopoly(**2**) was recovered from the reaction mixture in quantitative yield. On the other hand, the polymerization of tBMA successfully occurred to afford the poly(**2**-*b*-tBMA) possessing a predictable molecular weight and its narrow distribution. The SEC curve of the resulting block copolymer completely shifted from that of the starting poly(**2**) toward the higher molecular weight side, as can be seen in Figure 3. The nucleophilicity of the terminal carbanion derived from **2** is too low to react with styrene but sufficiently effective to initiate the polymerization of tBMA. It is demonstrated that the well-defined block copolymers of reversed sequence can be synthesized by the reversible sequential addition of **2** and tBMA.

Thus, we have demonstrated the polymerizability of a novel vinyl heterocyclic monomer under the anionic mechanism from the results on the block copolymerization of **2** and styrene or tBMA. These results on the crossover reaction also indicate that the anionic polymerizability of **2** is comparable to those of alkyl methacrylates. In monomer **2**, the electron-withdrawing C=N double bond of the oxazole function directly conjugates with the 2-substituted isopropenyl group to reduce the π-electron density (especially on the β-carbon), similar to the case of 2-vinyl- or 2-isopropenylpyridine. Since the benzoxazole moiety also provides an extended conjugation system containing ten π-electrons, the propagating terminal carbanion derived from **2** is stabilized by the resonance effect. It was previously reported that Q and e values of 2-vinyl-4,5-dimethyloxazole and 2-isopropenyl-4,5-dimethyloxazole were Q = 2.2, e = +0.40 and Q = 2.8, e = +0.24,[24] respectively. The large Q value and the positive e values for both monomers are away from the values of styrene (Q = 1.00, e = −0.80) and comparable to those of methyl methacrylate (Q = 0.74, e = 0.40). This clearly supports the extended resonance effect of the oxazole moiety and the low π-electron density of the carbon−carbon double bond, respectively. In particular, the latter e values indicate the high anionic polymerizability of vinylbenzoxazoles, **1** and **2**, as well as the vinyloxazole derivatives mentioned above.

In addition to these e values, it should be mentioned that the anionic polymerizabilities of these monomers

Table 4. Solubilities of Poly(1), Poly(2), Poly(2-vinylpyridine), and Polystyrene[a]

solvent	polymer			
	poly(**1**)	poly(**2**)	poly(2-vinyl-pyridine)	poly-styrene
hexane	I	I	I	I
benzene	S	S	S	S
diethyl ether	I	I	I	S
chloroform	S	S	S	S
acetone	S	S	S	S
ethyl acetate	S	S	S	S
pyridine	S	S	S	S
1,4-dioxane	S	I	S	S
tetrahydrofuran	S	S	S	S
N,*N*-dimethyl-formamide	S	S	S	S
dimethyl sulfoxide	I	I	S	I
ethanol	I	I	S	I
methanol	I	I	S	I
water	I	I	I	I
2 N HCl	I	I	S	I

[a] I, insoluble; S, soluble.

can be independently predicted by the chemical shift of the β-carbon of the vinyl group in ^{13}C NMR spectroscopy.[23] For example, the chemical shift of the β-carbon of α-methylstyrene, styrene, 4-cyanostyrene,[25] 2-vinylpyridine, methyl methacrylate, and methyl acrylate are known to be 112.4, 113.8, 117.6, 118.1, 125.1, and 129.9 ppm, respectively. It is obviously confirmed that the monomers having lower ^{13}C chemical shifts on the β-carbon actually show higher polymerizabilities under the anionic mechanism.[23] The values for **1** and **2** are 125.2 and 121.2 ppm and are ranked between those of 2-vinylpyridine and methyl methacrylate, supporting clearly the lowered π-electron density and the enhanced electrophilicity of the vinyl groups for **1** and **2**. The synthesis and the anionic polymerization of other vinyl heterocycles are in progress, and comprehensive discussion on the polymerizability of novel vinylheterocyclic monomers will be possible in the future.

The poly(**1**) and poly(**2**) obtained were white-yellow powders and could be cast into transparent films from their solutions. The solubility of the resulting polymers are listed in Table 4 along with those of poly(2-vinylpyridine) and polystyrene as references. Poly(**1**) and poly(**2**) are soluble in a wide variety of organic solvents and show solubilities similar to that of polystyrene. They are, however, insoluble in polar solvents such as dimethyl sulfoxide, ethanol, methanol, and 2 N HCl, which dissolve poly(2-vinylpyridine). This may indicate the lower polarity or basicity of the oxazole moiety than that of the pyridine ring. The glass transition temperatures (T_g's) of poly(**1**) and poly(**2**), measured by differential scanning calorimetry (DSC), were 112 and 195 °C, respectively.

In conclusion, we have succeeded in the anionic living polymerization of 2-isopropenylbenzoxazole (**2**) in THF at -78 °C to afford a polymer having a well-regulated chain length. On the other hand, the polymerization of the 2-vinyl counterpart, 2-vinylbenzoxazole (**1**), gave the polymers of broad MWDs under the same conditions. Substitution at the vinyl α-carbon was therefore essential to obtain a stable living polymer in the anionic polymerization of 2-vinylbenzoxazoles. The results of block copolymerization demonstrated that the anionic polymerizability of **2** was remarkably enhanced by the electron-withdrawing character of the benzoxazole moiety. The polymerizability of **2** was comparable to that of alkyl methacrylates under anionic conditions.

Experimental Section

Materials. Commercially available acryloyl chloride and methacryloyl chloride (Tokyo Kasei Co. Ltd.) were used without purification. 2-Aminophenol was recrystallized from methanol. α-Methylstyrene and styrene were distilled over CaH_2. These styrene monomers were further purified by distillation in the presence of phenylmagnesium chloride (THF solution) on a vacuum line. 1,1-Diphenylethylene (DPE) was purified by fractional distillation over CaH_2 and finally distilled from *n*-BuLi under vacuum. 1,1-Bis[4-(trimethylsilyl)phenyl]ethylene (TMS_2DPE) was synthesized by the Grignard reaction of 4-(trimethylsilyl)chlorobenzene and ethyl acetate and purified as previously reported.[25] *tert*-Butyl methacrylate (tBMA) was distilled over CaH_2 and finally distilled over trioctylaluminum on the vacuum line.[26] THF used as a polymerization solvent was refluxed over sodium wire for 5 h and distilled from lithium aluminum hydride and finally through a vacuum line from the sodium naphthalenide solution.

Initiators. Commercially available *s*-BuLi as a 1.05 M solution in cyclohexane was used without purification and diluted with heptane. Lithium naphthalenide and potassium naphthalenide were prepared by the reactions of a small excess amount of naphthalene with the corresponding alkali metal in dry THF. Potassium *tert*-butoxide (*t*-BuOK) was prepared from potassium naphthalenide and *tert*-butyl alcohol in THF. (Diphenylmethyl)potassium was prepared by the reaction of potassium naphthalenide and diphenylmethane in THF at room temperature for 3 days. (Triphenylmethyl)potassium was directly synthesized from potassium metal and triphenylmethane in THF at ambient temperature for 2 days. These initiators were sealed off under high vacuum conditions in ampules equipped with breakseals and stored at -30 °C. The concentrations of initiators were determined by colorimetric titration with standardized 1-octanol in a sealed reactor under high vacuum conditions.[27]

2-(*N*-Acryloylamino)phenol. To a stirred suspension of 2-aminophenol (31.8 g, 291 mmol) in 4% NaOH solution (300 mL) was added dropwise acryloyl chloride (25.0 g, 276 mmol) at 0 °C for 1 h. The reaction mixture was vigorously stirred at 0 °C for an additional 4 h and then poured into 100 mL of 6 N HCl with cooling. The mixture was extracted with ethyl acetate three times and dried over anhydrous $MgSO_4$. After concentration of the solution, the residue was purified by flash column chromatography (silica gel, hexane/ethyl acetate = 1/1) to give a crude crystal of 2-(*N*-acryloylamino)phenol (14.4 g, 88.3 mmol, 32%, mp 120−122 °C). 90 MHz ^{1}H NMR ($(CD_3)_2SO$): δ 5.74 and 6.14 (2d, 2H, J = 10 and 17 Hz, $=CH_2$), 6.54−7.85 (m, 5H, $-CH=$ and aromatic), 9.50 (s, 1H, CONH), 9.84 (s, 1H, OH).

2-(*N*-Methacryloylamino)phenol.[28] To a stirred solution of 2-aminophenol (28.4 g, 261 mmol), pyridine (21 mL), and DMF (300 mL) was added dropwise methacryloyl chloride (25.0 g, 258 mmol) in DMF (40 mL) at 0 °C for 1 h. The reaction mixture was stirred at 0 °C for an additional 4 h, and then most of pyridine and DMF was removed in vacuo from the mixture. The residue was diluted with 200 mL of Et_2O and washed with 2 N HCl (200 mL × 1) and water (200 mL × 2) and finally dried over anhydrous $MgSO_4$. Concentration of the solution gave a crude crystal of 2-(*N*-methacryloylamino)phenol (32.0 g, 181 mmol, 70%, mp 104−106 °C). 90 MHz ^{1}H NMR ($CDCl_3$): δ 2.10 (s, 1H, CH_3), 5.60 (s, 1H, cis $=CH_2$), 5.90 (s, 1H, trans $=CH_2$), 6.8−7.3 (m, 4H, aromatic), 7.80 (s, 1H, CONH), 8.65 (s, 1H, OH).

2-Vinylbenzoxazole (1).[29] A mixture of 2-(*N*-acryloylamino)phenol (12.4 g, 76.1 mmol), *p*-toluenesulfonic acid (0.22 g), *tert*-butylcatechol (10 mg), and xylene (300 mL) was heated for 6 h under reflux with azeotropic separation of water by means of a Dean-Stark water trap. After cooling, the reaction mixture was washed with 5% NaOH solution (100 mL × 1) and water (100 mL × 2) and then dried over anhydrous $MgSO_4$. After concentration of the solution, vacuum distillation gave a colorless liquid of **1** (5.33 g, 36.8 mmol, 48%, bp 68−69 °C/0.2 mmHg). The monomer was characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopies. 90 MHz ^{1}H NMR

($CDCl_3$): δ 5.85 and 6.45 (2d, 2H, J = 10 and 18 Hz, $=CH_2$), 6.79 (dd, 1H, $-CH=$), 7.23–7.77 (m, 4H, aromatic). 23 MHz ^{13}C NMR ($CDCl_3$): δ 110.5 (Ar, C5), 120.2 (Ar, C8), 123.9 ($=CH_2$), 124.4 and 125.4 (Ar, C6 and C7), 125.2 ($-CH=$), 141.8 (Ar, C4), 150.3 (Ar, C9), 162.0 (C=N). IR (KBr, cm^{-1}): 741, 772, 826, 935, 1243, 1453 (C=N), 1535.

2-Isopropenylbenzoxazole (2).[28] A mixture of 2-(*N*-methacryloylamino)phenol (32.0 g, 181 mmol), *p*-toluenesulfonic acid (0.40 g), *tert*-butylcatechol (10 mg), and xylene (200 mL) was heated for 30 h under reflux with azeotropic separation of water by means of a Dean-Stark water trap. After cooling and concentration of the reaction mixture, the residue was purified by flash column chromatography (silica gel, hexane/ethyl acetate = 9/1) to give a crude crystal of **2**. Recrystallizations from methanol and hexane gave a colorless crystal of **2** (9.38 g, 59.0 mmol, 33%, mp 38–39 °C). The monomer was characterized by ^1H NMR, ^{13}C NMR, and IR spectroscopies. 90 MHz ^1H NMR ($CDCl_3$): δ 2.29 (s, 3H, CH_3), 5.60 (s, 1H, cis $=CH_2$), 6.24 (s, 1H, trans $=CH_2$), 7.21–7.84 (m, 4H, aromatic). 23 MHz ^{13}C NMR ($CDCl_3$): δ 19.0 (CH_3), 110.3 (Ar, C5), 120.1 (Ar, C8), 121.2 ($=CH_2$), 124.2 and 125.2 (Ar, C6 and C7), 132.0 ($CH_3-C=$), 141.9 (Ar, C4), 150.5 (Ar, C9), 163.7 (C=N). IR (KBr, cm^{-1}): 741, 761, 813, 932, 1104, 1131, 1244, 1457 (C=N), 1537.

Purification. Liquid monomer **1** was purified by fractional distillations. Solid monomer **2** was recrystallized from methanol and hexane. The purified monomers were respectively sealed off under degassed conditions in an apparatus equipped with a breakseal in the presence of CaH_2 and heptane. The monomer solutions were stirred for 24 h at room temperature and distilled from CaH_2 on a vacuum line into ampules fitted with breakseals. Next, to remove impurities in the monomer, trioctylaluminum (1 mmol) in heptane was added to the monomer (ca. 30 mmol) at −78 °C. The mixture was then stirred for 0.5 h at ambient temperature under vacuum (10^{-6} mmHg). It was distilled again under vacuum conditions into an all-glass ampule equipped with a breakseal and then diluted with dry THF. The resulting monomer solutions (0.3–0.5 M in THF) were stored at −30 °C until ready to use for the anionic polymerization.

Polymerization Procedures. All polymerizations were carried out in an all-glass apparatus equipped with breakseals with vigorous shaking under high vacuum conditions, as previously reported.[27] The polymerization was terminated with degassed methanol. After polymerization, the reaction mixture was poured into a large excess of hexane to precipitate a polymer. The resulting polymers were purified by reprecipitations in THF/hexane and then by freeze-drying from the benzene solution. The polymer was then characterized by ^1H and ^{13}C NMR and IR spectroscopies. The following is the full list.

Poly(1): 90 MHz ^1H NMR ($CDCl_3$) δ 1.6–2.6 (broad, 2H, CH_2), 2.7–3.2 (broad, 1H, CH), 6.6–7.4 (broad, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 34–39 (CH_2CH), 110.1 (Ar, C5), 119.3 (Ar, C8), 123.7 and 124.3 (Ar, C6 and C7), 140.7 (Ar, C4), 150.2 (Ar, C9), 167.0 (C=N); IR (KBr, cm^{-1}) 751, 763, 910, 925, 1003, 1144, 1245, 1453, 1571, 1613, 2930.

Poly(2): 90 MHz ^1H NMR ($CDCl_3$) δ 0.1–1.1 (CH_3), 1.4–2.8 (CH_2), 6.2–7.8 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 18–22 (CH_3), 40.5 (CH_3-C) 55–57 (CH_2), 110.3 (Ar, C5), 119.7 (Ar, C8), 124.1 and 124.6 (Ar, C6 and C7), 140.9 (Ar, C4), 149.9 (Ar, C9), 169–171 (C=N); IR (KBr, cm^{-1}) 865, 990, 1055, 1127, 1210, 1297, 1389, 1511.

Typical Procedure of Block Copolymerization. In an all-glass apparatus in vacuo, the first-stage polymerization of **2** (4.27 mmol) was initiated with (triphenylmethyl)potassium (0.0737 mmol) in THF at −78 °C. After 1 h, a portion of living pre-poly(**2**) (0.0439 mmol) was withdrawn to determine the characteristics of the first-stage polymer. To the residue of the polymerization system was added tBMA (7.33 mmol) in THF at −78 °C in one portion with vigorous stirring, and the mixture was reacted for 1 h to complete the second-stage polymerization. After quenching with degassed methanol, both polymers were obtained in quantitative yield. Both homopoly(**2**) and poly(**2**-*b*-tBMA) possessed the predicted molecular weights and narrow MWDs, as shown in Table 3 (run 23). Similarly, the sequential copolymerization of tBMA and **2** could quantitatively proceed to afford a well-defined block copolymer by the reversed addition of the both comonomers.

Measurements. Infrared spectra (KBr disk) were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz ^1H, 22.53 MHz ^{13}C) in $CDCl_3$. Chemical shifts were reported in ppm downfield relative to tetramethylsilane (δ 0) for ^1H NMR and to $CDCl_3$ (δ 77.1) for ^{13}C NMR as standards. Size exclusion chromatograms (SEC) for MWD determination were obtained at 40 °C with a TOSOH HLC-8020 instrument equipped with three polystyrene gel columns (TOSOH G5000H_{XL}, G4000H_{XL}, and G3000H_{XL}) with ultraviolet (254 nm) or refractive index detection. THF was a carrier solvent at a flow rate of 1.0 mL min^{-1}. The glass transition temperatures of the polymers were measured by differential scanning calorimetry using a Seiko Instrument DSC220 apparatus and analyzed by an SSC5200TA station. The samples were first heated to 220 °C, cooled rapidly to −20 °C, and then scanned again at a rate of 20 °C/min.

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